WO01105599

Publication Title:

IMAGE RECEIVING ELEMENT AND METHOD OF MANUFACTURING THE ELEMENT

Abstract:

Abstract of WO0105599

An ink jet recording sheet and method of manufacture wherein a recording composition of a binder, silica pigment particles, and cationic organosilane coupling agent is coated onto a substrate with the silica pigment particles and cationic organosilane coupling agent added as separate constituents to form the recording composition. Data supplied from the esp@cenet database - Worldwide

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
25 January 2001 (25.01.2001)

PCT

(10) International Publication Number
WO 01/05599 A1

(51) International Patent Classification[7]: B41M 5/00

(21) International Application Number: PCT/US00/01501

(22) International Filing Date: 21 January 2000 (21.01.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/357,338 14 July 1999 (14.07.1999) US

(71) Applicant: IMATION CORP. [US/US]; 1 Imation Place, P.O. Box 64898, Saint Paul, MN 55164-0898 (US).

(72) Inventors: YARMEY, Susan, K.; P.O. Box 64898, Saint Paul, MN 55164-0898 (US). STEINER, Michael, L.; P.O. Box 64898, Saint Paul, MN 55164-0898 (US).

(74) Agents: BUHARIN, Amelia, A. et al.; Imation Legal Affairs, P.O. Box 64898, Saint Paul, MN 55164-0898 (US).

(81) Designated State *(national)*: JP.

(84) Designated States *(regional)*: European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published:
— *With international search report.*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/05599 A1

(54) Title: IMAGE RECEIVING ELEMENT AND METHOD OF MANUFACTURING THE ELEMENT

(57) Abstract: An ink jet recording sheet and method of manufacture wherein a recording composition of a binder, silica pigment particles, and cationic organosilane coupling agent is coated onto a substrate with the silica pigment particles and cationic organosilane coupling agent added as separate constituents to form the recording composition.

IMAGE RECEIVING ELEMENT AND METHOD OF MANUFACTURING THE ELEMENT

FIELD OF THE INVENTION

The invention broadly relates to image receiving elements and methods of manufacturing such elements. More specifically, the invention relates to ink jet receptors, also known as ink jet recording sheets, and methods of manufacturing such elements.

BACKGROUND OF THE INVENTION

Ink jet printing is a printing technique in which images (*e.g.*, graphs, pictures, symbols, text, etc.) are produced by the ejection of uniformly shaped droplets of ink onto the receptor surface of a recording sheet. This printing technique is widely used in the personal and small office markets. Other applications include low end proofing, and medical referral markets.

The maximum image resolution and throughput of an ink jet printer are primarily determined by the size of the jetted drop and the rate of drop ejection. Several factors limit ink jet printers from attaining the maximum image resolution capable of being achieved by the printer. One of these limiting factors is the nature of the recording sheet receiving the jetted drops.

Investigators have found image quality to be directly related to the ink absorption rate of the receptor surface and the strength of the bond formed between the ink and the receptor, with image quality increasing with an increase in absorption rate and bond strength. As a general matter, investigators have found that when the ink droplets are not absorbed quickly enough, the ink tends to spread and interact with neighboring droplets of ink, resulting in such defects as feathering, pooling, or bleeding. Investigators have also found that when the ink is not strongly bonded to the receptor, the ink tends to bleed through the receptor and possess reduced resolution, reduced water fastness, and reduced smudge resistance. Such problems

are exacerbated as the droplet ejection frequency is increased for purposes of increasing throughput.

Ink receptor surfaces can be divided into two basic types: continuous phase systems and discontinuous phase systems. Continuous phase systems generally function by swelling to absorb water or ink deposited onto the receptor surface, with the rate of absorption determined by the chemical nature of the polymer used in the system. Typical polymers used in continuous phase systems include gelatins, polyvinyl alcohol, and cellulose. Exemplary continuous phase systems are discussed in United States Patents Nos. 3,889,270, 4,503,111, and 5,141,599.

While generally effective as an ink jet receptor surface, most polymeric continuous phase systems are water soluble, thereby reducing the waterfastness of the receptor. Some polymeric continuous phase systems have overcome the waterfastness issue by mixing an insoluble cross-linked polymer into the system (*e.g.*, forming a semi-interpenetrating network as described in United States Patents Nos. 5,342,688 and 5,389,723). However, the introduction of an insoluble cross-linked polymer into the system intrinsically reduces the absorption rate of the system.

Discontinuous phase systems function by providing pores within the receptor surface capable of absorbing ink by capillary forces. Discontinuous phase systems are generally preferred over continuous phase systems as they absorb ink considerably faster than continuous phase systems.

Discontinuous phase systems are divided into two basic types. A first type of a discontinuous phase system, known as a "porous discontinuous phase system", utilizes micron sized porous pigment particles in the recording layer for purposes of absorbing ink jetted onto the recording layer into the particles through a multitude of tiny interconnected pores in each particle. Ink recording sheets having a porous, discontinuous phase system recording layer are disclosed in United States Patent Nos. 5,165,973; 5,270,103; 5,397,619; 5,478,631; International Published Application WO 97 01448.

A second alternative type of discontinuous phase system, known as a "nonporous discontinuous phase system" utilizes nonporous pigment particles held

together by a polymeric binder in such a manner that interstitial voids are created between the pigment particles capable of absorbing ink jetted onto the receptor surface.

Ink jet recording sheets with a recording layer of the porous discontinuous phase system type generally provide good ink absorptivity and superior ink capacity, in exchange for some loss in the glossy appearance of the recording sheet. Alternatively, ink jet recording sheets with a recording layer of the nonporous discontinuous phase system type provide superior ink absorptivity and a glossy appearance in exchange for a limited ink capacity due to practical limitations upon the thickness of the coating.

Discontinuous phase system receptor surfaces often incorporate a mordant or dye fixing agent for purposes of binding the dye molecules adsorbed within the pores of the receptor surface. A number of different types of mordants have been used, including neutral silane coupling agents, such as disclosed in JP 8164667 (polyalkylene oxide silane), JP 3218887 (silicon compounds), JP 62178384 (silane coupling agents) and JP 60224580 (silane coupling agents with chloro, amino, aminoethyl or vinyl functionality); and monomers, oligomers and polymers of primary, secondary and tertiary amines and quaternary ammonium salts, such as disclosed in United States Patents Nos. 5,302 and 5,750,200 437.

While neutral silane coupling agents, cationic monomeric, oligomeric and polymeric amines, and quaternary ammonium salts are generally effective for providing improved bonding between the ink and the receptor surface, a substantial need continues to exist for a mordant providing further improved bonding of ink by the receptor layer while maintaining a superior ink absorption rate and ink absorption capacity.

SUMMARY OF THE INVENTION

A first embodiment of the invention is an ink jet recording sheet providing superior bonding of ink by the receptor layer while maintaining a superior

ink absorption rate and ink absorption capacity, comprising a receptor layer of a binder, pigment particles, and a cationic organosilane coupling agent.

A second embodiment of the invention is a method of making an ink jet recording sheet comprising (1) coating a layer of a recording composition on a major surfaces of a substrate wherein the recording composition is a dispersion containing at least (i) a binder, (ii) silica pigment particles, and (iii) a cationic organosilane coupling agent, with the silica pigment particles and cationic organosilane coupling agent added as separate constituents, and (2) drying the recording layer.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is an enlarged side view of an end of one embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

Nomenclature

10	Ink Jet Recording Sheet
20	Substrate
30	Subbing Layer
40	Recording Layer
50	Anti-curling Layer

Definitions

As utilized herein, including the claims, the term "**thickness**", when used in connection with the recording layer, means the thickness of the recording layer on a dry basis.

As utilized herein, including the claims, "**wt%**" is based upon the solids content of the composition (*i.e.*, calculated on a dry basis).

Construction

The discontinuous ink jet recording sheet **10** includes a coating of a discontinuous recording layer **40** on a suitable substrate **20**, wherein the recording layer **40** strongly bonds dye absorbed within the interstices of the recording layer **40** while maintaining superior ink absorptivity and capacity.

SUBSTRATE

The substrate **20** may be any of the typical materials used in the construction of ink jet recording sheets capable of providing the necessary visual appearance and structural support for the recording layer(s) **40**. Examples of suitable substrates include paper, cloth, polymers, metals, and glass. Thin flexible sheets are generally preferred, with paper the substrate of choice when an opaque support is desired, and polymeric films used when a translucent or transparent appearance is desired. The thickness of the substrate **20** is preferably in the range of about 0.05 to 1.0 mm.

SUBBING LAYER

The major surface of the substrate **20** to be coated with the recording layer **40** may optionally be treated with a subbing layer **30**, such as a primer or an antistatic layer, before the recording layer **40** is coated onto the substrate **20**.

RECORDING LAYER

The recording layer **40** is comprised of pigment particles treated with a cationic organosilane coupling agent and held together by a binder. The recording layer **40** should have a thickness of greater than about 30 μm in order to provide sufficient capacity. Recording layers **40** possessing an acceptable appearance can be formed up to a thickness of about 100 μm, with a thickness of between about 35 to 85 μm preferred.

Pigment Particles

The recording layer **40** contains pigment particles of the type conventionally used in ink jet recording layers, including specifically, but not exclusively, (i) inorganic pigments such as alumina, aluminum hydroxide, aluminum oxide, aluminum silicate, barium sulfate, calcium carbonate, calcium silicate, calcium sulfate, kaolin, magnesium silicate, amorphous silica, colloidal silica, silicic acid, sodium silicate, talc, titania, titanium dioxide, zinc carbonate, and zinc oxide, and (ii) organic pigments such as styrene and acrylic plastic pigments, urea resin pigments, and melamine resin. The cationic silane coupling agents are particularly suited for use in connection with silica and silicate particles as the cationic silane coupling agents can form a strong bond with the surface of the particles and effectively convert the normally anionic surface of the particles to a cationic surface capable of electrostatically attracting ink jet dyes.

Pigment particles having an average particle size of less than about 500 nm are capable of producing a recording layer **40** having the desired appearance and performance. Pigment particles having an average particle size of between about 10 -500 nm are generally preferred, with particles having an average particle size of between about 50 -300 nm desired and particles having an average particle size of between about 50 -100 nm favored.

The pigment particles can be of substantially any desired shape, with symmetrical particles, particularly spherical particles, generally preferred as they enhance the performance characteristics of the recording layer **40**.

Binder

The pigment particles are held together by a binder. The binder is provided in an amount sufficient to hold the pigment particles together and provide an acceptable appearance, while leaving pores (*i.e.*, interconnected interstitial voids) within the recording layer **40** to enhance performance. Ink jetted onto the recording layer **40** will be channeled into and stored within the pores in the layer **40** through capillary action.

Substantially any of the conventional binders may be employed, including specifically, but not exclusively: starch derivatives such as oxidized starch, etherified starch and phosphate starch; cellulose derivatives such as carboxymethyl cellulose and hydroxymethyl cellulose; conjugated diene-type copolymer latexes such as styrene-butadiene and methyl methacrylate-butadiene copolymers; acrylic polymer resins and latexes such as polymers and copolymers of acrylic and methacrylic acid esters; vinyl-type polymer latexes such as ethylene-vinyl acetate copolymer; the aforementioned latexes modified to include a functional group such as a carboxyl group; aqueous adhesives such as melamine or urea resins; synthetic resins such as polyurethanes, unsaturated polyesters, vinyl chloride-vinyl acetate copolymer, polyvinyl butyral and alkyd resins; casein, gelatin, soybean protein, polyvinyl alcohol and derivatives thereof, polyvinyl pyrolidone, and maleic anhydride resins.

Relative Concentrations of Pigment Particles and Binder

The amount of binder used in the recording layer **40** relative to the amount of pigment particles should be selected to balance the competing interests of integrity and wear resistance (enhanced by increased amounts of binder) with ink absorption rate and ink absorption capacity (enhanced by decreased amounts of binder). Hence, a careful consideration of binder concentration is important to create a suitable ink jet recording layer **40** having a proper balance of performance characteristics. As a general matter, a weight ratio of pigment to binder of about 1:2 to 20:1, preferably about 2:1 to 10:1, provides acceptable balancing of the competing performance characteristics.

Cationic Silane Coupling Agent

The cationic organosilane coupling agent includes a first moiety (R') capable of dissociating in water to produce a positively charged group on the organosilane coupling agent, and a second moiety (R") effective for bonding to the pigment particles. When dissociated, the first moiety is effective for electrostatically attracting and forming an insoluble salt with dyes having an electron donating group

(*e.g.*, an -S03$^-$) such as is present on many of the Azo, direct and acid dyes typical of ink jet inks.

Preferred cationic silane coupling agents possesses the basic structure:

$$R' \, L \, Si \, R''_3$$

wherein: **(i)** R' is a quaternary ammonium group, **(ii)** L is a single bond or divalent linking group, and **(ii)** each R" is independently an alkoxy.

A more preferred cationic organosilane coupling agent has the basic structure:

$$R'_n \, Si \, R''_{(4-n)}$$

wherein: **(i)** R' is $-LN^+R^3_3$ where L is a single bond or divalent linking group, and each R^3 is independently hydrogen, alkyl, aryl or alkaryl with at least two R^3 being alkyl, aryl or alkaryl, **(ii)** each R" is independently an alkoxy; and **(iii)** n is 1 or 2.

Exemplary suitable cationic organosilane coupling agents include specifically, but not exclusively,

N,N-didecyl-N-methyl-N-(3-trimethoxysilylpropyl) ammonium chloride, octadecyldimethyl (3-trimethoxysilylpropyl) ammonium chloride, N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride, tetradecyldimethyl (3-trimethoxysilylpropyl) ammonium chloride, N-trimethoxysilylethyl benzyl-N,N,N-trimethyl ammonium chloride, N-(trimethoxysilylpropyl) isothiouronium chloride, N-trimethoxysilylpropyl-N,N,N-tri-n-butyl ammonium chloride, N-trimethoxysilylpropyl-N,N,N-tri-n-butyl ammonium bromide, 3-[2-N-benzylaminoethylaminopropyl] trimethoxysilane hydrochloride, N-(3-trimethoxysilylpropyl)-N-methyl-N,N-diallyl ammonium chloride, and 3-N-styrylmethyl-2-aminoethylamino-propyltrimethoxysilane hydrochloride.

Additives

Other typical additives such as surfactants, plasticizers, antistatic agents, buffers, coating aids, matting agents, particulates for managing mechanical processing of the ink jet recording sheet, hardeners, colorants, viscosity modifiers, preservatives, and the like may optionally be incorporated into the ink jet recording layer as desired.

ANTI-CURLING LAYER

An anti-curl layer **50** may optionally be coated on the back side of the substrate **20**.

Method of Manufacture

BLENDING OF CONSTITUENTS

The constituents of the recording layer may be blended together by substantially any convenient method. Exemplary procedures include, (i) sequentially charging pigment, silane coupling agent and binder into a sufficient quantity of solvent (preferably water) under constant agitation, (ii) simultaneously charging the pigment, silane coupling agent and binder with sufficient solvent into a suitable mixer, (iii) dispersing the pigment in water, adding the silane coupling agent to the aqueous dispersion of pigment, drying the dispersion to form silane treated pigment particles and then adding the silane treated pigment particles to an aqueous dispersion of the binder, and (iv) dispersing the pigment in water, adding the silane coupling agent to the aqueous dispersion of pigment, and then adding the silane-containing aqueous dispersion of pigment into an aqueous dispersion of the binder. Regardless of the specific method employed, it is believed that the silane coupling agent associates with the pigment particles by the development of an ionic and/or hydrogen bond between the silane coupling agent to the pigment.

Coating and Drying of Recording Layer

The recording layer may be coated by any of the conventional techniques for coating such materials, including specifically, but not exclusively, extrusion coating, direct and indirect gravure coating, knife coating, Mayer rod coating, roll coating, etc.

Similarly, the coated recording layer may be dried by any of the conventional techniques for drying such coated recording layers.

Optional Processing

The recording layer **40** can be calendared to improve gloss, with the calendar rolls heated or unheated and rotating concurrent or countercurrent with respect to movement of the ink jet recording sheet **10**. Care must be taken to avoid excessively compressing the film so as not to decrease the porosity and thereby the performance of the recording layer **40**.

Experimental

Glossary

Airflex 500	A nonionic latex of ethylene vinyl acetate copolymer having an average particle size of 170 nm and a T_g of 5 °C available from Air Products of Allentown, Pennsylvania.
Epson Stylus® Color 800 Printer	Ink jet printer available from Epson America, Inc. of Torrence, CA.
Epson Stylus® 800 Color Ink	Color ink jet cartridge containing cyan, magenta and yellow available from Epson America, Inc. of Torrence, CA under model number S020089.
Epson Stylus® 800 Black Ink	Black ink jet cartridge available from Epson America, Inc. of Torrence, CA under model number S020108.
MP1040	Particulate silica having a diameter of 100±30 nm available from Nissan Chemical Industries, Ltd. of Tokyo, Japan.

PET	Polyethylene Terephthalate
PVDC	Polyvinylidenecholoride
T_g	Glass transition temperature
3-aminopropyltrimethoxy silane	A nonionic silane available from Acros Organics of New Jersey under catalog number 15108-1000.
diphenyldiethoxysilane	A nonionic silane available from Gelest, Inc. of Tullytown, PA under catalog number SID 4525.0.
N-3-trimethoxysilyl-propyl-ethylene diamine	A nonionic silane available from Acros Organics of New Jersey under catalog number 21653-1000.
Octadecyltrimethoxysilane	A nonionic silane available from Aldrich Chemical Company, Inc. of Milwaukee, WI under catalog number 37,621-3.
Vinyltrimethoxysilane	A nonionic silane available from Acros Organics of New Jersey under catalog number 21652-1000.
3-trimethoxysilyl propyl methacrylate	A nonionic silane available from Acros Organics of New Jersey under catalog number 21655-1000.
3-chloropropyltriethoxy silane	A nonionic silane available from Aldrich Chemical Company, Inc. of Milwaukee, WI under catalog number 43,568-6.
Phenyltrimethoxysilane	A nonionic silane available from Hus Petrarch Systems of Bristo, PA under catalog number P0330.
N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride	A cationic silane available from Gelest, Inc. of Tullytown, PA under catalog number SIT 8395.0.
N-trimethoxysilylethyl benzyl-N,N,N-trimethyl ammonium chloride	A cationic silane available from Gelest, Inc. of Tullytown, PA under catalog number SIS 6994.0.

3-N-styrylmethyl-2-amino-ethylamino-propyltrimethoxy-silane hydrochloride	A cationic silane available from Gelest, Inc. of Tullytown, PA under catalog number SIT 8415.0.

Testing Procedures

COLOR DENSITY

Epson Stylus® Color 800™ ink is jetted from an Epson Stylus® Color 800™ printer onto the recording layer of the sample sheet in step patches ranging from 0 (no color) to 16 (full color saturation). Printed samples with midtone patches (i.e., patches between 4 and 8) were selected for testing unless otherwise noted. Color density is measured with a Gretag™ spectrophotometer as the log of the ratio of the intensity of visible light given out by the bulb in the spectrophotometer over the intensity of visible light reflected by the printed sample. The color density is recorded.

DROP SIZE

Epson Stylus® Color 800™ ink is jetted from an Epson Stylus® Color 800™ printer onto the recording layer of the sample sheet for a midtone patch. Drop size of the jetted ink is viewed through a microscope, aimed perpendicular to the surface of the recording layer, giving a top view of the ink drop absorbed into the layer. The microscope is attached to a video camera and frame-grabber capable of permitting computer analysis and storage of the image. Computer analysis of the image yields drop size, with the average of approximately twenty five drops reported as the drop size for the sample.

Standard Sample Construction

Into a beaker equipped with a magnetic stirrer was placed deionized water and an organic silane of the type and in the amount set forth in Table One to form a silane solution. Into the stirred silane solution was added MP1040™ in the amount set forth in Table One, to form a silica dispersion. The silica dispersion was stirred overnight at approximately 80°C (176°F). Into the stirred silica dispersion

was added Airflex™ 500 in the amount set forth in Table One, to form a final dispersion. The final dispersion was stirred for several hours prior to coating.

The stirred final dispersion was coated onto a PVDC primed PET sheet using a knife coater with a seven millimeter gap. The coated PET sheet was oven dried at 120°F (49°C) for seven minutes to form an ink jet recording sheet with a recording layer.

Examples

COMPARATIVE EXAMPLES C2, C3 AND C4
EXAMPLES 2 AND 3
(Color Saturation)
(Nonionic Silane Coupling Agents -v- Cationic Silane Coupling Agents)

Sample ink jet recording sheets having a recording layer containing a silane coupling agent were constructed in accordance with the Standard Sample Construction Procedure. The color saturation of the sample recording sheets was tested in accordance with the Color Saturation Testing Protocol. Drop size was tested in accordance with the Drop Size Testing Protocol. The results of the testing were recorded, and are set forth in Tables Two and Three respectively.

As shown in Table Two, color saturation is generally improved for recording sheets having a recording layer containing a cationic silane coupling agent when compared to nonionic silane coupling agents, with the greatest improvement observed when conducting high density ink jet printing. Without intending to be unduly limited thereby, we believe that this increase in color saturation is due to the ability to retain the dye proximate the surface of the recording sheet due to an ionic attraction between the cationic silane coupling agent in the recording layer and the dye.

COMPARATIVE EXAMPLES $C1_{low}$, $C1_{med}$, $C1_{high}$
EXAMPLES 1_{low}, 1_{med} 1_{high}
(Color Saturation and Drop Size)
(Different Concentrations of Cationic Silane Coupling Agents)

Ink jet recording sheets having a recording layer containing different concentrations of a silane coupling agent were constructed in accordance with the Standard Sample Construction Procedure. The color saturation of the recording sheets were tested in accordance with the Color Saturation Testing Protocol. Drop size was also tested in accordance with the Drop Size Determination Protocol. The results of the testing were recorded, and are set forth in Tables Two and Three respectively.

As shown in Table Three, color saturation is generally improved for recording sheets having a recording layer containing a cationic silane coupling agent when compared to nonionic silane coupling agents, with little change in color saturation over the concentration range of silane coupling agent studied.

TABLE ONE

(Composition of Ink Jet Receptor Layer)

Sample	Deionized H_2O (grams)	Silane Coupling Agent		MP 1040 (Silica) (grams)	Airflex 500 (Latex Binder) (grams)	pH	Stable Dispersion (Yes/No)
		Type	(grams)				
Comparative Examples *(Nonionic Silanes)*							
$C1_{low}$	6.36	3-aminopropyltrimethoxysilane	0.49	30	3.64	Neutral	Yes
$C1_{med}$	6.36	3-aminopropyltrimethoxysilane	0.98	30	3.64	Neutral	Yes
$C1_{high}$	6.36	3-aminopropyltrimethoxysilane	2.94	30	3.64	Neutral	Yes
C2	6.36	diphenyldiethoxysilane	0.60	30	3.64	Neutral	Yes
C3	6.36	N-3-trimethoxysilyl-propyl-ethylene diamine	0.50	30	3.64	Neutral	Yes
C4	6.36	octadecyltrimethoxysilane	0.91	30	3.64	Neutral	No
						Acidic†	Yes

Sample	Deionized H_2O (grams)	Silane Coupling Agent Type	Silane Coupling Agent (grams)	MP 1040 (Silica) (grams)	Airflex 500 (Latex Binder) (grams)	pH	Stable Dispersion (Yes/No)
C5	6.36	vinyltrimethoxysilane	0.33	30	3.64	Neutral	No
						Acidic†	No
C6	6.36	3-trimethoxysilyl propyl methacrylate	0.91	30	3.64	Neutral	No
						Acidic†	No
C7	6.36	3-chloropropyltriethoxysilane	0.53	30	3.64	Neutral	No
						Acidic†	No
C8	6.36	phenyltrimethoxysilane	0.43	30	3.64	Neutral	No
						Acidic†	No
(Cationic Silanes)							
1_{low}	6.36	N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride	1.13	30	3.64	Neutral	Yes
1_{med}	6.36	N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride	2.26	30	3.64	Neutral	Yes
1_{high}	6.36	N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride	6.78	30	3.64	Neutral	Yes
2	6.36	N-trimethoxysilylethylbenzyl-N,N,N-trimethylammonium chloride	1.46	30	3.64	Neutral	Yes

Sample	Deionized H_2O (grams)	Silane Coupling Agent		MP 1040 (Silica) (grams)	Airflex 500 (Latex Binder) (grams)	pH	Stable Dispersion (Yes/No)
		Type	(grams)				
3	6.36	3-N-styrylmethyl-2-aminoethylamino-propyltrimethoxysilane hydrochloride	1.64	30	3.64	Neutral	Yes

† Glacial Acetic Acid (0.69 grams) added.

TABLE TWO

(COLOR SATURATION)

Sample	Step Patch (0-16)	Color Density			
		Black	Cyan	Magenta	Yellow
Comparative Examples *(Nonionic Silanes)*					
$C1_{low}$	6	0.52	0.68	0.52	0.55
	10	0.74	1.05	0.71	0.65
	14	1.02	1.23	0.85	0.76
	16	1.35	1.29	0.97	0.86
$C1_{med}$	6	0.59	0.83	0.62	0.56
	10	0.79	1.26	0.80	0.78
	14	1.09	1.31	0.93	0.81
	16	1.60	1.34	1.20	0.80
$C1_{high}$	6	0.53	0.83	0.49	0.47
	10	0.81	1.12	0.75	0.61
	14	1.21	1.32	1.09	0.78
	16	1.48	1.49	1.33	1.04

Sample	Step Patch (0-16)	Color Density			
		Black	Cyan	Magenta	Yellow
C2	6	0.56	0.83	0.53	0.70
	10	0.61	1.07	0.64	0.71
	14	0.86	1.09	0.63	0.71
	16	1.26	1.12	0.89	0.71
C3	6	0.47	0.57	0.49	0.38
	10	0.85	1.17	0.86	0.77
	14	1.08	1.46	0.90	0.89
	16	1.28	1.41	0.98	0.93
C4	6	0.47	0.63	0.43	0.67
	10	0.65	0.87	0.62	0.88
	14	0.99	1.24	0.76	0.92
	16	1.39	1.28	1.05	0.94
(Cationic Silanes)					
1_{low}	6	0.78	1.41	0.59	0.67
	10	1.13	1.51	0.70	0.77
	14	1.41	1.59	0.94	0.89
	16	1.77	1.84	1.19	1.04

Sample	Step Patch (0-16)	Color Density			
		Black	Cyan	Magenta	Yellow
1_{med}	6	0.73	0.76	0.66	0.5
	10	1.05	1.23	0.88	0.65
	14	1.33	1.51	1.03	0.65
	16	1.74	1.85	1.44	0.69
1_{high}	6	0.61	0.85	0.55	0.63
	10	0.83	1.27	0.82	0.90
	14	1.27	1.36	1.66	1.14
	16	1.76	1.64	1.95	1.43
2	6	0.56	0.70	0.57	0.52
	10	1.05	1.49	0.99	0.98
	14	1.37	1.91	1.12	1.03
	16	1.70	1.93	1.24	1.12
3	6	0.54	0.63	0.55	0.47
	10	0.99	1.27	0.96	0.90
	14	1.27	1.64	1.05	1.04
	16	1.51	1.64	1.16	1.03

TABLE THREE

(DROP SIZE)

Sample	Drop Size	
	Cyan (μm^2)	Magenta (μm^2)
Comparative Examples *(Nonionic Silanes)*		
$C1_{low}$	7,500	7,800
$C1_{med}$	7,300	7,500
$C1_{high}$	7,000	7,300
C2	13,300	10,100
C3	7,500	10,400
C4	14,000	9,000
(Cationic Silanes)		
1_{low}	5,800	7,800
1_{med}	5,700	6,400
1_{high}	5,300	5,800
2	4,300	5,100
3	7,200	6,600

We claim:

1. An ink jet recording sheet comprising:
   (a) a substrate having first and second major surfaces, and
   (b) a recording layer on at least one of the major surfaces of the substrate comprising at least:
      (1) a binder,
      (2) silica pigment particles, and
      (3) a cationic organosilane coupling agent.

2. The ink jet recording sheet of claim 1 wherein the cationic organosilane coupling agent has the structure:

$$R' \, L \, Si \, R''_3$$

wherein: **(i)** R' is a quaternary ammonium group, **(ii)** L is a single bond or divalent linking group, and **(iii)** each R" is independently an alkoxy.

3. The ink jet recording sheet of claim 1 wherein the cationic organosilane coupling agent has the structure:

$$R'_n \, Si \, R''_{(4-n)}$$

wherein: **(i)** R' is $-LN^+R^3_3$ where L is a single bond or divalent linking group, and each R^3 is independently hydrogen, alkyl, aryl or alkaryl with at least two R^3 being alkyl, aryl or alkaryl, **(ii)** each R" is independently an alkoxy; and **(iii)** n is 1 or 2.

4. The ink jet recording sheet of claim 3 wherein **(i)** each R" is independently a C_{1-3} alkoxy, and **(ii)** n is 1.

5. The ink jet recording sheet of claims 1 to 4 wherein at least a portion of the cationic organosilane coupling agent is associated with the silica pigment particles.

6. The ink jet recording sheet of claims 1 to 5 wherein the cationic organosilane coupling agent associated with the silica pigment particles is chemically bonded to the silica pigment particle.

7. The ink jet recording sheet of claims 1 to 6 wherein the substrate is a paper substrate.

8. A method of making an ink jet recording sheet comprising:

(a) obtaining a substrate having first and second major surfaces,

(b) coating a layer of a recording composition on at least one of the major surfaces of the substrate wherein the recording composition is a dispersion containing at least (i) a binder, (ii) silica pigment particles, and (iii) a cationic organosilane coupling agent, with the silica pigment particles and cationic organosilane coupling agent added as separate constituents, and

(c) drying the recording layer.

9. The method of claim 8 wherein at least a portion of the cationic organosilane coupling agent is associated with the silica pigment particles after the cationic organosilane coupling agent and silica pigment particles are added to the dispersion.

10. The method of claim 8 wherein the substrate is a paper substrate.

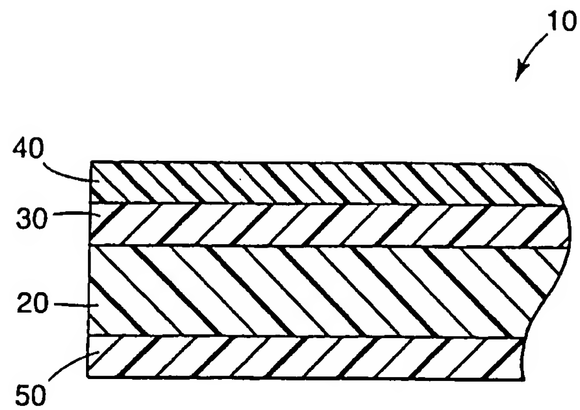

Fig. 1

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/01501

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B41M5/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B41M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMICAL ABSTRACTS, vol. 124, no. 22, 27 May 1996 (1996-05-27) Columbus, Ohio, US; abstract no. 302644, KOBAYASHI, TAKASHI ET AL: "Water-resistant recording sheet having ammonium silane coupling agent-treated surface" XP002137624 abstract & JP 08 034160 A (FUJI PHOTO FILM CO LTD, JAPAN) 6 February 1996 (1996-02-06) examples --- -/--	1-10

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
17 May 2000	29/05/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Markham, R

1

Inte)onal Application No
PCT/US 00/01501

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMICAL ABSTRACTS, vol. 112, no. 20, 14 May 1990 (1990-05-14) Columbus, Ohio, US; abstract no. 189150, SAITO, MASAKO ET AL: "Receptor for water-thinned ink-jet recording and recording on it" XP002137626 abstract & JP 01 281982 A (CANON K. K., JAPAN) 13 November 1989 (1989-11-13)	1-10
L	CHEMICAL ABSTRACTS, vol. 132, no. 4, 24 January 2000 (2000-01-24) Columbus, Ohio, US; abstract no. 42856, FUCHISAWA, TETSUO ET AL: "Ink-jet recording sheets and their manufacture" XP002137625 abstract	1-10
P,X	& JP 11 348416 A (FUJI PHOTO FILM CO., LTD., JAPAN) 21 December 1999 (1999-12-21) example 9	
A	DATABASE WPI Section Ch, Week 199851 Derwent Publications Ltd., London, GB; Class A26, AN 1998-602716 XP002137627 & JP 10 272834 A (TORAY IND INC), 13 October 1998 (1998-10-13) abstract	1,8
A	DATABASE WPI Section Ch, Week 198450 Derwent Publications Ltd., London, GB; Class A82, AN 1984-309109 XP002137628 & JP 59 192589 A (MATSUSHITA ELEC IND CO LTD), 31 October 1984 (1984-10-31) abstract	1,8

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte ional Application No
PCT/US 00/01501

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 8034160 A	06-02-1996	NONE	
JP 1281982 A	13-11-1989	NONE	
JP 11348416 A	21-12-1999	NONE	
JP 10272834 A	13-10-1998	NONE	
JP 59192589 A	31-10-1984	JP 1019353 B	11-04-1989
		JP 1536019 C	21-12-1989